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Complete arsenic removal from water using biocatalytic systems based on anaerobic films grown on carbon fibers

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ABSTRACT

Arsenic is a hazardous metalloid with potentially negative impacts on both the environment and human health. Current methods of arsenic remediation are expensive and can cause secondary contamination. In this paper we explore the potential of using bioelectrochemical systems (a group of environmentally friendly bio-based technologies with great potential for bioremediation and waste valorisation) for arsenic removal. Previous studies have reported that the spontaneous oxidation of As(III) to As(V) was completely realized in bioelectrochemical systems, however, any of the them succeeded in removing the total arsenic concentration. This study demonstrates that not only it is possible to oxidize As(III) to As(V), but also the total elimination of arsenic can be achieved as the result of intracellular accumulation.

1. Introduction

Arsenic is a carcinogenic metalloid that it is mainly present in the environment due to geogenic sources and anthropogenic activities. Water-soil interactions that take place within aquifers result in the release of arsenic contained in mineral compounds, leading to groundwater contamination and threatening the health of millions of animals and humans worldwide [1]. Health problems produced by high concentrations of arsenic include skin, liver, and lung cancer, and haematological, renal, and respiratory diseases [2]. Inorganic As(III) and As(V) are the most common forms in water and they have different modes of toxicity, although As(III) are the most toxic species due to As(III) binds to sulfhydryl groups of proteins, affecting their structure or catalytic capabilities [3,4].

Many methods have been studied and used for the removal of arsenic species, including adsorption, precipitation with Fe(III), and chemical oxidation [5]. However, these methods have a high cost and can cause secondary contamination. Therefore, alternatives have been sought, among which microbiological processes such as bioelectrochemical systems (BES) stand out. These systems are attracting increased attention, since they are able to remove contaminants while generating electricity simultaneously, offering an economical way of providing sustainable energy and environmental protection [6,7]. Previous studies have reported a complete spontaneous oxidation of As(III) can take place during seven days of operation in single-chamber microbial fuel cells [8], and demonstrated as well the anaerobic microbiological oxidation of As(III) with a polarized electrode serving as the sole terminal electron acceptor [9]. Additional investigations have reported electroactive microorganisms could successively remove As released from soils when an organic carbon source was supplied [10]. However, none of the studies in the literature have succeeded in removing the total arsenic concentration in oligotrophic environment like groundwater, so far.

The BES anode material should allow bacteria to form electroactive biofilm and, therefore, should be conductive and noncorrosive and have good biocompatibility and large surface area [11]. Carbon-based materials meet many of these requirements, and this has made them the most widely used electrode material. Carbon cloth, carbon felt, graphite granules, graphite plates, graphite felt, graphite brushes, graphite rods, carbon brushes and carbon nanotubes have been some of these

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carbon-based materials used as anode in BES. Among these ones, carbon felt has been one of the most widely used as anode due to their good electronic conduction, high surface area and strong biocompatibility [12]. Nevertheless, in the current study we bet for the use of carbon fibres as support for the biocatalytic film, based on our previously reported investigations about the electrochemical properties of these carbon-based materials [13]. Thus, the main objective of the present research has been to develop an alternative method for the treatment of water contaminated with As(III) using a bioelectrochemical system (BES), supported on well electrochemically defined carbon fibres. The approach has consisted in achieving the As(III) catalytic oxidation to As (V) and the entire elimination of the latter species from the water by the carbon fibres-supported BES. For this purpose, the following have been investigated: (i) the spontaneous oxidation of As(III) to As(IV) in the anodic chamber of the novel biocatalytic system developed, (ii) the nature of the microorganism community present in this system and the identity of the main one responsible for As oxidation, and (iii) the effect of the open circuit, in the electrical connection, on the biocatalytic behaviour.

2. Materials and methods

2.1. Carbon fibers-supported biocatalytic film

The carbon material used as support for the biocatalytic film consisted of non-corrosive graphite fibres disposed as a brush (Mill-Rose, USA), perpendicularly distributed around a twisted titanium wire of 15 cm length, giving rise to a cylindric carbon brush with 10 cm of outer diameter. These graphite fibres are highly conductive, presenting an open structure that avoids biofouling, and with a fractal dimension greater than 2 consistent with an efficient electrode. The electroactive area determined for the carbon brush employed as anode is 66 cm^2; the highest one compared with other carbon-based anodes tested including brush, felt or paper formats; and the highest apparent surface area (5.33 cm^2) resulting in an electroactive area/apparent surface ratio of 12 [13]. The latter value was also higher than that obtained in other materials such as carbon paper or some types of carbon felt. The type of carbon brush employed in the present study also showed the lowest mean ohmic drop (8 Ω), due to the lowest ohmic resistance, and the most enhanced electrode kinetics, due to the widest range of scan rate (up to 200 mV $\cdot s^{-1}$) for which the response of peak reduction currents remains linear with respect to the variation of the square root of the scan rate [13]. This implies the absence of irreversibility phenomena up to 200 mV$\cdot s^{-1}$ for the carbon brush anode employed, contrary to what was found for many other carbon-based anodes such as other carbon brushes, thick and fine carbon felts, or carbon papers [13]. Detailed procedures and equations for calculating the data provided above in this 2.1 section are found in a previously reported work [13].

The source of inoculum, used to grow biocatalytic film on the carbon fibres, was sludge with a high metal load sampled in the village *Aviados*, in *León* province (Spain). This sludge was diluted in a culture medium (dilution rate 1:2). containing 100 mg L^{-1} KH_2PO_4, 10 mg L^{-1} $CaCl_2$, 100 mg L^{-1} $(NH_4)_2SO_4$, 500 mg L^{-1} $NaHCO_3$, 1 ml L^{-1} of metals solution and 1 ml L^{-1} of vitamins solution. This medium had an approximate conductivity of 700 μS cm^{-1}.

The procedure for the acclimation of the biocatalytic system supported on the carbon fibres was carried out during five weeks, replacing 100 ml of medium by 100 ml of fresh medium every week. This acclimation promoted the formation of an active biofilm. Once a steady state was reached, batch tests were performed.

2.2. BES set up and operation

The assays were carried out in duplicate using H-type reactors with a volume of 500 ml per chamber (Adams & Chittenden Scientific, CA, USA). These reactors are constructed on two standard borosilicate media bottles with a total volume of 1 L (500 ml per anode and 500 ml per cathode) and fitted with GL14 threaded glass side ports. Tooled glass flanges, with seals and wraparound knuckle clamps. Were used to connect both chambers. The anode chamber and the cathode chamber were separated by an anion exchange membrane (Membranes International, USA) to prevent the diffusion of arsenic cations between chambers. The electrodes that form the anode and cathode were made of carbon and platinum, respectively. The platinum mesh had a projected area of 4 cm^2 (2 ×2 cm). Two of the four reactors worked in microbial fuel cell (MFC) mode, where the electrodes were connected to a resistor of 1000 Ω during start-up, and 10 Ω during operation. The other two reactors worked at open circuit voltage (OCV), where there was no electrical connection between the anode and cathode.

Bicarbonate was used as the sole carbon source. A phosphate buffer solution (0.1 M) was used as a catholyte. Considering previous studies [9,14], the concentration of arsenic in the anolyte was fixed at 10 mg L^{-1} and was added in the form of $NaAsO_2$. Therefore, at the beginning of the experiments all the arsenic was in the form of As(III).

After previous probes to estimate the most appropriate duration for the biocatalytic tests, the limit for the batch time of all the experiments presented in this study was fixed in 35 days.

2.3. Chemical and microscopy analysis

Samples were centrifuged at 4800 ppm for 5 min for arsenic analysis. Subsequently, two aliquots were taken. To both aliquots, 10 μL of 37% HCl and 400 μL of a 10% L-cysteine monohydrate solution in 0.01 M HCl were added, but only one of them was placed in a 90 °C oven for 60 min. From the first aliquot we obtained the value of the concentration of As (III) and from the second aliquot we acquired the value of the sum of the concentrations of As(III) and As(V). Both samples were measured in an inductively coupled plasma optical emission spectrometer, 5100 ICP-OES (Agilent, USA), using a 1.5% sodium borohydride and 0.5% NaOH solution.

For microscopic analysis, the electrode fibres were carefully cut after the reactor was disassembled, washed with distilled water, and then dried at room temperature. Before the microstructure was observed using a scanning electron microscope (SEM) JSM-6480LV microscope (JEOL, Japan), the fibres were coated with a thin layer of gold in a sputter coater (EM ACE200, Leica Microsystems, Switzerland). The elemental components of the electrode surface were analysed using an INCA energy dispersive X-ray detector (EDX) INCA (Oxford Instrument, UK), which is integrated in the SEM equipment.

2.4. Microbial community analysis

After a reactivity experiment was completed, the analysis of the microbial community was performed following a previously reported method [15]. For this purpose, a portion of carbon fibres was cut using sterilised scissors according to the procedure used by San-Martín et al. [16]. Genomic DNA from the sampled electrode was extracted using the PowerSoil® DNA Isolation Kit (MoBio Laboratories Inc., USA), following the manufacturer's instructions.

The entire DNA extract was used for the pyrosequencing of 16S-rRNA gene-based massive library, targeting the eubacterial region V1–V3 16S-rRNA, and performed at MR DNA (www.mrdnalab.com, USA), utilising MiSeq equipment (Illumina, USA). The primer set used was 27Fmod (5′-AGRGTTTGATCMTGGCTCAG-3′)/519 R modBio (5′-GTNTTACNGCGGCKGCTG-3′). Diluted DNA extracts were used as a template for polymerase chain reactions. The obtained DNA reads were compiled in FASTq files for further bioinformatics processing. The trimming of the 16S-rRNA bar-coded sequences into libraries was carried out using QIIME software. Quality filtering of the reads was performed at Q25 quality prior to grouping into operational taxonomic units (OTUs) at a 97% sequence homology cut-off. The sequencing quality score of a given base, Q, is defined by the following equation:

Q= −10 $\log_{10}P$, where "*P*" is the probability of the base to be called incorrectly.

3. Results and discussion

3.1. As(III) oxidation using BES

The evolutions of the relative concentrations of As(III), As(V), and As (total) in the reaction medium, with the operation time in the open circuit (OCV) or the microbial fuel cell (MFC) systems, are displayed in Fig. 1. In both systems, the concentration of As(III), as the nominal arsenic species, decreases in favour of the rise in the concentration of As (V), according to the oxidation process expected. Additionally, as the As (III) oxidation begins, a consumption of As is observed in both systems (Fig. 1a and b) with the lowering of the total concentration of As. Nevertheless, the rates of either As(III) oxidation or As(total) intake, as well as the maximum threshold values for the latter, are totally different depending on whether or not there is electrical connection between electrodes. Thus, the zero relative concentration of As(III) is approached (*ca.* 0.05) in 10 operation days within the microbial fuel cell system (Fig. 1b), while for the open circuit (OCV) system (Fig. 1a) more than 30 days were needed to approach an equivalent zero concentration. Accordingly, the relative concentration of As(V) in the MFC system reaches the maximum during the 10th operation day, while for the open circuit system this maximum appears as the asymptotic limit for the 35 days operation range.

With respect to the relative concentration of the total As content, in general, it starts decreasing looking for the meeting point with the As(V) maximum concentration in both systems studied. Thus, this point is not crossed within the whole operation range in the open circuit system, due to the asymptotic evolution of the As(V) concentration which is inversely followed by the As total concentration. Consequently, the arsenic intake is slow in the open circuit and it does not exceed the 25% for the 35 days operation period. On the contrary, in the MFC system, the Arsenic intake meets the maximum of As(V) relative concentration at the 10th day, after which the As total relative concentration keeps decreasing overlapping the downwards evolution of the As(V) relative concentration.

The arsenic elimination from the aqueous reaction medium was complete for an operation period of 20 days in the MFC closed circuit, after total oxidation of As(III) into As(V) occurred during the first 10 days of operation. Therefore, we can confirm that the As(III) passes into the form of an As(V) before being eliminated.

In general, the processes for the As removal using BES could include precipitation or adsorption on the electrode surface, or absorption by entering the cathode chamber through the anion exchange membrane. In our specific case, As(V) removal by adsorption on the surface electrode is not expected to have a significant contribution, since previous studies using similar carbon-based anodes stated no arsenic adsorption observed on anodes such as graphite [9] or graphene [17]. Indeed, elemental analysis, by energy-dispersive X-ray spectroscopy (EDX) on selected areas over scanning electron micrography images of our electrodes after the 35 h reactivity test showed no more than 2 wt%. of arsenic.

Therefore, we can conclude that arsenic removal in the MFC occurs by absorption and not by adsorption and that only the As(V) passes from the medium to the microorganisms on the anode surface, which we will discuss in the next section.

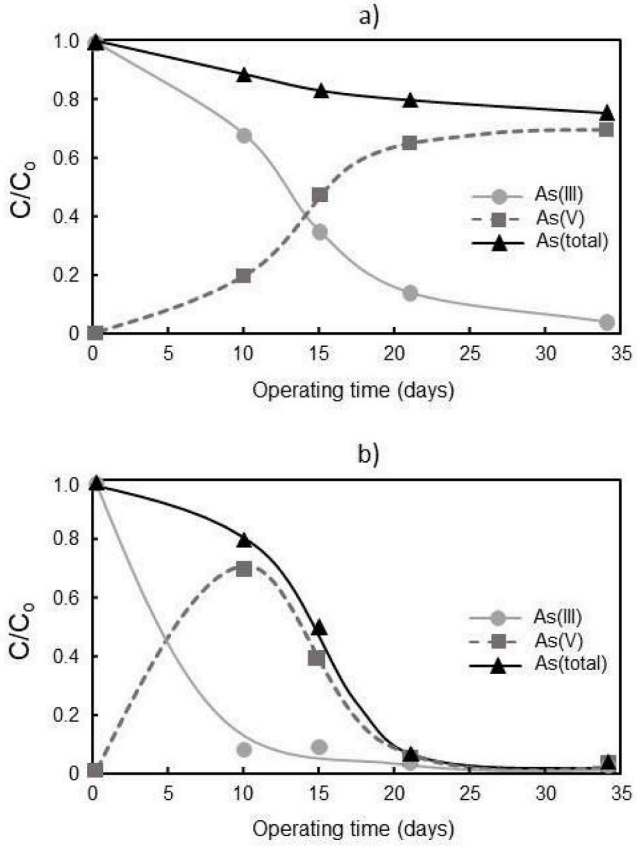

Fig. 1. Evolution of relative concentration of As(III), As(V) and As(total) in the reaction medium during batch operation for the OCV system (a), and for the MFC system (b). The concentration of arsenic at the beginning of the test was fixed at 10 mg L^{-1}.

3.2. Bacterial community involved in arsenic oxidation

Genomic analyses of the microbial community present in the pristine inoculum, as well as in the OCV and MFC systems after the experiment for the As elimination during 35 days was finished, were carried out and their results are shown in Fig. 2. Concretely, this figure displays the relative abundances of the 16S-rRNA sequences found in each of the three cases (pristine inoculum, OCV, MFC) at phylum and family levels.

Relative abundance of each phylum has been calculated as the ratio of the absolute abundance of the phylum to the total absolute abundance of all phyla. In all the samples, the six dominant phyla were *Proteobacteria, Bacteroides, Chloroflexi, Firmicutes, Spirochaetaceae, and Acidobacteria*. In this sense, it is important to point out that gene homologues encoding *AioBA* (arsenic (III) oxidase) have been found in phylogenetically diverse strains including members of the *Proteobacteria,*

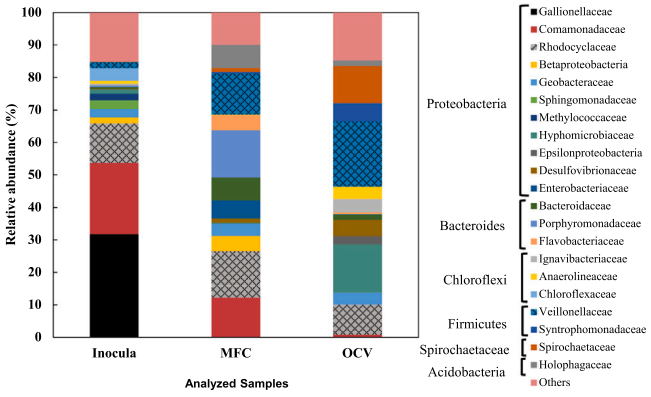

Fig. 2. Relative abundances (%) of dominant families in the pristine inoculum, and the biofilms in MFC and OCV systems after 35 operating days. The families in the graph legend, clustered into phylum, have been ordered (from top to bottom) according to appearance order (from bottom to top) in the graph columns.

Bacteroides, Chloroflexi, and Firmicutes [18], *i.e.*, the first four dominant phyla present in the bacterial community showing the effective biocatalytic performance in As oxidation and elimination (Fig. 1) Although, there is still no specific information at this respect for *Spirochaetacea* and *Acidobacteria*, it cannot be completely ruled out since Yamamura and Amachi (2014) showed that the diversity of *AioBA* genes in prokaryotes is wider than previously suspected.

From the six dominant phyla found, *Proteobacteria* was the most abundant in all three samples, although its relative content underwent strong variation decreasing from over 75% in the pristine inoculum to less than 45%, in both OCV and MFC systems, after 35 days of operation. The decrease in Proteobacteria worked in favour of *Bacteroides* or *Firmicutes* after the operation modes of MFC or OCV, respectively. These results agree with previous studies [19], where a high content of *Proteobacteria* was found in a very acid and metal-rich medium, like our inoculum, which later provided a gap for *Bacteroides* in the biofilm of our reactors designed for arsenic oxidation in more neutral conditions (pH= 7.8 ± 0.3),. In addition, the percentage of *Firmicutes* in the OCV system is very similar to that obtained in previous studies with comparable operating conditions [20].

Gallionella, belonging to the so-called iron bacteria, is undoubtedly the dominant genus in the pristine inoculum at genera level, according to the relative abundance results displayed in Fig. 3. Its main habitats are ferruginous mineral springs, waterworks, and wells [21]. However, its presence is reduced to zero in our systems (both MFC and OCV). This bacterium is able to catalyze the oxidation of Fe (II) to Fe (III) and of using reduced sulfur compounds (sulfur and thiosulfate) as electron donors and energy sources [22]. In addition, it contributes to the immobilization of arsenic through its ability to form solid (hydro)oxides of Fe [23] and has genes encoding the arsenate-reductase ArsC and the arsenite transporter ArsB [24]. Nevertheless, the change to more neutral conditions (pH= 7.8 ± 0.3) undergone during the reactivity experiments probably impeded its growth.

Contrary to expectations, the dominant genus for the two systems operated (OCV and MFC) is the same: *Zymophilus*, which has a relative abundance of 17% and 12% for the OCV and MFC, respectively. Although *Zymophilus* is not a frequent genus in bioelectrochemical systems, however, it can be occasionally found, as confirmed in several studies [25]. The role of this genus as an arsenic transporter has been defined [26], and this may be the reason for their high relative abundance in both reactors with high arsenic concentration. The second most abundant genus in the MFC was *Curvibacter* (10%), which has the genes *aioAB*, *arrB*, *arsR*, *arsA*, and *arsB* [27]. The *aio* genes are responsible for the oxidation of As(III), while *arr* genes are responsible for As(V) respiration, and *ars* genes are responsible for the intracellular reduction of As(V). The presence of these genes may explain the elimination of arsenic in the effluent of the system operated in MFC, where As(III) was oxidized to As(V) and this was subsequently eliminated from the environment.

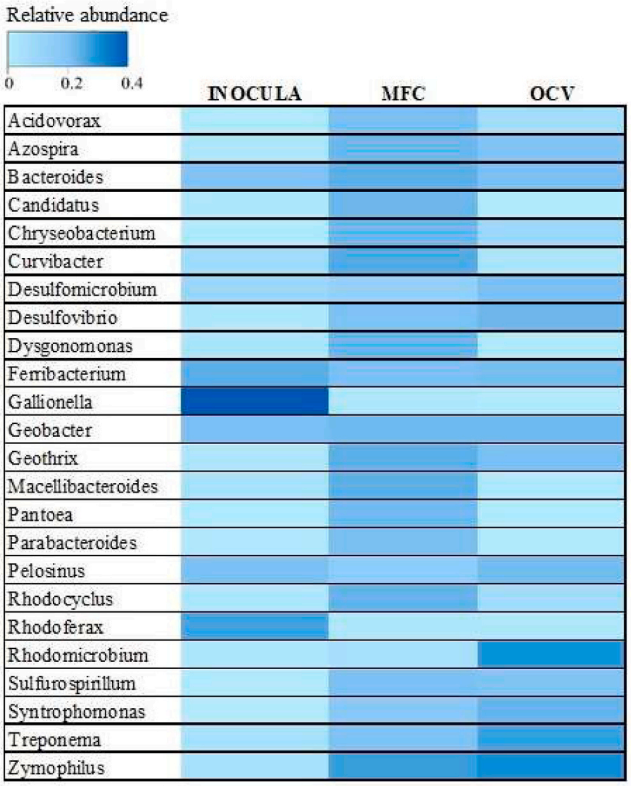

Fig. 3. Heat map summarizing the relative abundance (between 0 and 1) of the main genera present in the pristine inoculum, and the biofilms in MFC and OCV systems after 35 operating days. The maximum for the relative abundance range in the graph legend has been set up according to the highest relative abundance registered among the analyzed genera.

4. Conclusions

The results here exposed has demonstrated the high bioelectrochemical activity of the chosen biocatalytic films supported on non-corrosive graphite carbon fibers to spontaneously oxidize As(III) into As(V) and subsequently remove it from contaminated groundwater. For the system connected in MFC mode, total oxidation of As(III) to As (V) is achieved after 10 days of operation in the anodic chamber of the novel biocatalytic system developed. In addition, after 10 more days of operation, the total As concentration is eliminated by almost 100%. The results combination leads to the conclusion that using sludge with a high metal load as inoculum, allows the development of an anodic biofilm capable of totally oxidizing As(III) and consuming the As(V) by intracellular accumulation. The absence of a closed circuit in the electrical connection seems to affect bioremediation capacity, since the OCV system does not allow the development of *Curvibacter*, appearing as responsible to eliminate arsenic from the environment in MFC mode. Nevertheless, the OCV system studied also gave rise to developing bacteria capable of oxidizing As(III) to As(V), reducing the toxicity almost totally after an operation period of 20 days.

CRediT authorship contribution statement

M. Isabel San-Martín: Conceptualization, Investigation, Writing – original draft. **Raúl M. Alonso**: Methodology, Validation, Investigation. **Francisco Ivars-Barceló**: Conceptualization, Writing – review & editing, Funding acquisition. **Adrián Escapa**: Conceptualization, Writing – review & editing. **Antonio Morán**: Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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